UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

PROJECT REPORT
Colombia Investigations
(IR) CO-25

STATUS OF GEOCHEMICAL EXPLORATION IN COLOMBIA

by

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U. S. Geological Survey

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Prepared on behalf of the
Government of Colombia and the
Agency for International Development
U. S. Department of State

FEBRUARY 1972

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ABSTRACT

Geochemical exploration in Colombia was started by the Colombian Government in 1969 and is being conducted in five separate regions. In this program stream silt and pan concentrates of stream sediments are collected at widely spaced intervals as a means of reconnaissance mineral exploration. These samples are analyzed in Bogotá either by spectrograph or by atomic absorption. This program so far has resulted in the discovery of one ore deposit west of Ibague at Salento and in the mapping of numerous geochemical anomalies that have not yet been evaluated. No attempt has been made to use water analysis, and only a few experiments have been made in the use of soil analysis to obtain additional information about the geochemical anomalies. The large igneous intrusions of Colombia are covered by a deep soil which obscures indications of veins, hydrothermal alteration, small porphyry intrusions and other evidence of mineralization. It is possible that the geochemical program may discover a porphyry-type copper deposit in one of these intrusions.

INTRODUCTION

In Colombia all geochemical exploration studies have been made by the governmental Instituto Nacional de Investigaciones Geológico-Mineras (Ingeominas). Ingeominas is giving increasing emphasis to geochemical exploration and other direct methods of ore finding, and geochemical investigations have been undertaken in five different regions or zones (fig. 1).

My assignment in Colombia, from July 14 to September 16, 1971, to study these geochemical exploration programs in operation and to make suggestions concerning their continuance, was part of the mineral exploration program being conducted cooperatively by Ingeominas and the U. S. Geological Survey (USGS), sponsored by the Government of Colombia and the Agency for International Development (AID), U. S. Department of State, under PASA No. LA(IC) 40-71.

An itinerary for my tour of duty was prepared by Sr. Andrés Jimeno V., Director of Ingeominas, and by Mr. Earl M. Irving, geologist in charge of the USGS geological program in Colombia. I visited each of the five regions and have briefly described geochemical investigations made in each herein. The laboratory that analyzed the geochemical samples in Bogotá has been described previously by Rader (1970); some comments are included here to update the earlier report. Appended to this report is information on collecting samples, analyzing samples, and interpreting the reports statistically.

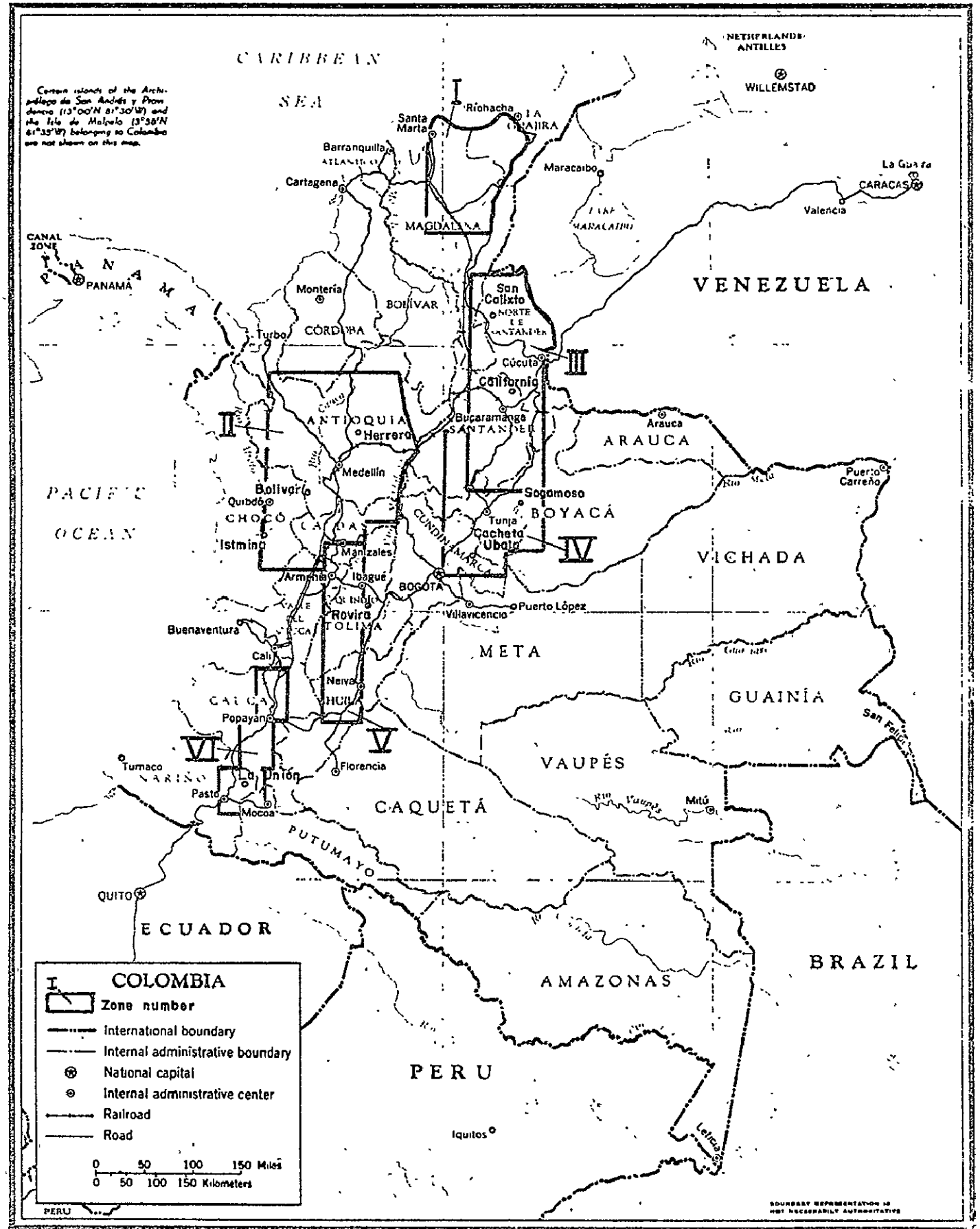

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Figure 1. Index map of Colombia showing location of Zones I-VI.

I am greatly indebted to Sr. Jaime Cruz, sub-Director of Ingeominas, who accompanied me on all my trips outside of Bogotá, and made all the necessary travel arrangements. Sr. Cruz speaks excellent English and served as interpreter when necessary. I would like to thank my Colombian friends for the excellent cooperation which I received everywhere during my visit.

GEOCHEMICAL INVESTIGATIONS IN FIVE REGIONS

Ibague (Zone V)

Geochemical investigations near Ibague (Zone V) (see fig. 1) have been conducted by Srs. Dario Barrero and Taissir Kassem, both of whom explained the results to the writer in the office and on field trips. Their initial study, which started during 1969 at Salento (Dept. of Quindio), resulted in the successful discovery of an ore deposit.

In the high, partially glaciated Salento district (Barrero and others, 1971), pan concentrates of stream sediments yielded grains of sphalerite, galena, argentite, and native silver. Analyses of these samples yielded interesting geochemical maps. One sample contained 5,000 ppm of lead. A geologic examination of the anomalous area discovered a lead-rich vein. Later exploration has revealed about 500,000 tons of ore having a value of more than $1,000,000. A mine is now under development.

Geochemical exploration in the Ibague region has been conducted in four other areas. The area near Rovira, just south of Ibague, is interesting because of the possibility of finding a concealed porphyry copper deposit. Here the bedrock is the Payande quartz diorite batholith of post-Cretaceous age. Dikes and small intrusions of porphyry are known from outcrops along roads and in stream beds. The deep soil prevents detailed mapping of the uplands.

In localities near Rovira visited by the writer, anomalous amounts of copper, molybdenum, tin, and tungsten have been found in stream-sediment samples. Both silt and nonmagnetic heavy minerals have high copper contents (up to 5,000 ppm). The only visible evidence of mineralization consists of narrow veinlets containing quartz, pink orthoclase, epidote, and a little molybdenite. The stream sediments contain many gossan fragments.

The streams in this area are intrenched about 100 meters in a mudflow which once covered the entire lowland. At altitudes above the top of the mudflow the bedrock is very deeply weathered. From these physiographic relations, I judge that the level of supergene enrichment for any concealed copper deposit would be about 100 meters above stream level. A suggestion was made to use stream silt and base-of-slope soil sampling to obtain additional data on copper. Anomalous areas probably will have to be investigated eventually by drills placed on the uplands. The stream valleys are more accessible but are beneath the probable level of an enriched ore body.

Medellín (Zone II)

Geologic investigations of the Cordillera Occidental (Zone II) are especially difficult because of the poor accessibility, high rainfall, and dense tropical forest. The rocks here are more mafic than those elsewhere in Colombia; Zone II contains greywacke and other marine strata interbedded with basalt. Some gabbro intrusions are present.

As explained by Sr. Alfonso Arias, the investigation of this zone consisted of collecting stream sediment samples along 17 traverses across the Cordillera. The most interesting results obtained so far appear to be copper anomalies in the northern part of the zone in an area mapped as granodiorite. More geochemical work to investigate these anomalies is desirable.

I collected soil samples at two small vein-type copper deposits to demonstrate how soil sampling can be used to investigate prospects. One of these is near Herrero and the other west of the town of Bolivar. The simple geochemical map made in connection with the soil sampling for the Herrero prospect indicates that the present tunneling is too far from the discovery outcrop.

Our party also visited the famous Chocó platinum deposits near Istima. All the platinum mined here comes from placer deposits. These deposits have been mined for centuries, but platinum has not yet been observed in the bedrock, and its lithologic source is unknown.

The new analytical methods devised by the USGS for determining platinum in trace amounts may be useful in investigating these deposits further, possibly as a collaborative investigation involving a Colombian geologist and one from the USGS. I suggest that pebble samples (100 small pebbles) be collected at various stream-sediment sample sites in the platiniferous area. The pebbles can be studied in the field and also in the USGS laboratories in Denver. In Denver the pebbles can be divided into lithologic groups, which can be analyzed separately. The

objective would be to show which type of rock, gabbro or other, contains the platinum. Such investigation may permit locating the source of the platinum and possibly lead to mining of the bedrock.

Popayan (Zone VI)

Near Popayan (Zone VI) stream silt and pan concentrates have been collected from around five igneous intrusions, most of which are quartz diorites. The stream silt was analyzed spectrographically, some of the samples were reported to contain as much as 1,000 ppm antimony. Most of the unexpectedly high antimony values are in samples that are also high in chromium. It is possible that a spectrographic line for chromium is being confused with a nearby antimony line. These samples should be reanalyzed by the independent colorimetric method for antimony. As equipment for making this colorimetric analysis is not available in Colombia, I took representative samples to Denver for analysis; colorimetric analyses of 26 samples were sent to Colombia on October 4, 1971. They show an antimony content of no more than 1 ppm.

Guided by Srs. Ignacio Cucalón H., Luis Albino Leon S., and Abigail Orrego L., I examined several of the igneous intrusions, which are all deeply weathered. We also visited an antimony mine east of La Unión (La Magdalena region). Here veins rich in stibnite occur in Tertiary volcanic rock. Geochemical study of such deposits would be greatly facilitated if equipment for the USGS colorimetric test for antimony were available. In epithermal deposits, antimony is likely to be associated with mercury and arsenic. Facilities are available now in Bogotá for determining arsenic, and it is planned to obtain a sensitive meter for determining mercury within 6 months.

Bucaramanga (Zone III)

Geochemical exploration near Bucaramanga (Zone III) has consisted of sampling silt from streams draining sedimentary rocks both north and south of Bucaramanga. These samples have been analyzed by the atomic absorption method in Bogotá. Some samples have also been analyzed colorimetrically at the Bucaramanga office by Sr. Dario Monsalve P., chemist.

Guided by Sr. Noel Téllez I., our party visited an area of detailed study near San Calixto where copper anomalies of as much as 62 ppm have been found along the contact of Jurassic redbeds and Cretaceous limestone. In one anomalous area, malachite is present along joints in volcanic rocks at the top of the Jurassic beds. Sr. Monsalve demonstrated his field kit for determining copper; it works very well even though the copper content of the sediment there is not high. As the copper is widely dispersed, and relatively low in amount, there seems to be little chance of finding minable deposits in this sedimentary sequence. Investigation of the granitic intrusions in this district may be more rewarding.

The ancient California gold district also was visited. The gold there is in quartz pyrite veins in metamorphic rock and has been mined since colonial times. Some mining is still in progress. In addition to the mines we examined two small stamp mills and one water-powered arrastra in operation. On a hike upstream from the village of California we tested drainage water from small creeks and various mine openings for copper and sulfate content. Our tests showed that oxidizing pyrite in veins yield some waters rich in sulfate. Thus a geochemical study of water (sulfate,

acidity, total heavy metal, etc.) might identify the main concentrations of pyrite. As the gold is associated with the pyrite, such a study might indicate the main concentrations of gold.

Sogamoso (Zone IV)

In Zone IV near the towns of Gachetá and Ubalá, vein-type deposits of sphalerite and galena occur in Lower Cretaceous calcareous shale, sandstone, and limestone. This area has been studied geochemically by collecting stream silt samples and analyzing them by atomic absorption. The results are given in a report by Srs. Luis E. Castillo P. and Alvaro Guerra Zea (1971).

Several deposits in this area were visited with Srs. Guerra, Erasmo Rodriguez, and Ricardo Camacho. In one area near Gachetá, where stream silt contains as much as 260 ppm zinc, the only identified source of zinc is a little sphalerite in concretions. Near Ubalá, soil samples were collected near a zinc vein to show how they can be used to trace veins in soil-covered areas. Another deposit visited was that at La Playa (not on fig. 1) where a high-grade block of sphalerite and siderite is within a large landslide. One silt sample taken near this block contained 2,300 ppm zinc. Much of the area investigated appears to have a metal content too low to be of economic significance. I suggested more soil sampling near known mineral deposits to provide a better basis for evaluating geochemical anomalies.

GEOCHEMICAL LABORATORY IN BOGOTA

The chemical laboratory is on the campus of the National University within a short walking distance to the main office of Ingeominas. This laboratory has been described by USGS chemists L. F. Rader, Jr., and A. T. Myers (1970). The equipment includes one 1.5-meter Jarrell Ash spectrograph and one Perkin Elmer Model 303 atomic absorption instrument. Most of the recommendations made by Rader and Myers have been followed, and the laboratory generally operates satisfactorily. Spectrographic analyses (22 elements per sample) are made at the rate of about 50 samples per day. Atomic absorption analyses (for copper, lead, and zinc in each sample) are made at the rate of about 80 samples per day. Molybdenum can be determined colorimetrically in the solution prepared for atomic absorption analysis.

Some difficulty has been encountered in obtaining supplies for the spectrograph. Prior to August 10, 1971, when spectrographic film was received from A. T. Myers, the spectrograph had not operated for two months because of lack of film. Equipment and chemicals for some colorimetric tests are lacking. For example, no Pyrex test tubes are available for tests that require fusions. One of these is the colorimetric test for antimony, which is needed to investigate antimony deposits south of Popayan. Much of the needed equipment and supplies is inexpensive; difficulties in ordering rather than cost appear to be the main reason the equipment and supplies are not available.

This laboratory no doubt will be dependent upon continuing assistance to obtain supplies and to improve techniques. Plans are in progress to obtain a USGS-type sensitive mercury meter. Such meters are expensive ($5,000) but are essential for determining mercury in trace amounts. Probably the laboratory should be equipped to detect trace amounts of gold and tellurium. Such analyses can be done with the present atomic-absorption instrument, but sample digestion probably would require better hoods.

Rader and Myers recommended that a sample preparation room be provided for all samples requiring trace analysis. The room should contain a crusher and several types of grinding devices. To date (1971) this room has not been provided. At present, samples for spectrographic analysis are prepared by hand grinding a very small amount of the sample. Without doubt the errors involved are large and could be decreased by mechanical grinding.

To facilitate operation of this chemical laboratory, it is recommended that Sr. Roberto Gaitan, who is in charge of this laboratory, visit the laboratory of the USGS Geochemical Exploration Branch in Denver. Other chemists, such as Srs. Alvaro Vargas C. and Hector Lozano V., are prospective trainees but have had difficulty satisfying the AID English-language requirements. A. P. Marranzino, USGS, has arranged to have some Colombian chemists receive training in a USGS-sponsored laboratory in Puerto Rico, where there are Spanish-speaking chemists.

RECOMMENDATIONS FOR INGEOMINAS

Much progress has been made by Ingeominas during the two years that the geochemical program has been in operation. Some of the anomalies investigated are too faint to be of possible economic importance. As the geologists gain experience in geochemistry, they will be able to judge better what kind of anomaly may indicate a valuable ore deposit.

The igneous intrusions and their border zones appear to be the best places to search geochemically for copper and other ore deposits in Colombia. In these intrusions, deep weathering tends to conceal porphyry, gossan, hydrothermal alteration, and supergene ore minerals that otherwise would be used as guides to ore. Copper anomalies found by stream sediment sampling south of Ibague and north of Medellín should be investigated now by additional sampling (including soil sampling) to better delimit the mineralization.

Other rocks of possible interest include Cretaceous or older sedimentary strata and volcanic flows that may contain vein-type deposits. To evaluate these rocks better more sampling should be done near known mines and prospects. Areas of iron-stained rocks or other evidence of hydrothermal alteration should be sampled. Both soil and stream-sediment samples should be collected.

The poorest areas for geochemical study in Colombia appear to be the relatively unconsolidated sediments of Tertiary or later age. These areas can be omitted from consideration.

Geologists conducting geochemical exploration programs like to have analytical results available quickly for interpretation. These interpretations will lead in turn to additional sampling, so the spent time waiting for analysis limits progress. Some geologists at Ingeominas have had to wait 8 to 12 months for analyses. This long period has slowed progress and probably has caused the geologists to lose interest. Delays also cause unfortunate antagonism between geologists and chemists.

The USGS has similar problems that have never been completely solved. Delays can be decreased by: 1) increasing the capacity of the laboratory; 2) reducing the number of analyses requested; and 3) analyzing some samples in regional offices. The capacity of the laboratory in Bogotá cannot be increased without substantial cost; however, the other two methods can be used.

Both pan concentrates and silt have been collected at many sample sites. The pan concentrates have been further concentrated by use of heavy liquids, and separated into magnetic and nonmagnetic fractions before analysis. Thus three types of sample have been obtained from many of the sample sites, and these have been analyzed separately. Making three separate analyses for each sample site requires much analytical work.

In the search for copper, lead, or zinc deposits, silt samples are more useful than pan concentrates. The silt samples have a metal content somewhat like that of the concentrates, but they are more representative of the average rock composition in the drainage basin. Another advantage of silt samples is that they can be analyzed conveniently by atomic absorption. For these and other reasons, it is suggested that silt samples

be used wherever possible, and that pan concentrates be used only for special studies (exploration for tin, tungsten, chromium, etc.). Some suggestions for collecting silt and other type of samples are given in Appendix I.

The USGS uses temporary laboratories in many areas of geochemical sampling. Samples are analyzed in these laboratories within a few days after collection; thus, if an anomalous sample is identified by analysis, it is a simple matter to collect more samples to confirm the anomaly. As geochemical sampling becomes more detailed in Colombia, and as the need grows for rapid analysis of many soil samples, small laboratories at the regional offices of Ingeominas probably will be required.

The total heavy-metal test using dithizone is ideal for use in a regional laboratory. I took a kit for making this test to Colombia, and demonstrated its use several times. The kit was left with Sr. Gabriel Paris for use in the Popayan office. Instructions on the use of this kit are given in Appendix II. Instructions for other simple geochemical prospecting tests have been given by Ward and others (1963).

All geologists involved in the Colombian geochemical program have a marked interest in applying statistics to the interpretation of the geochemical data. For most analyses, "rounded" values reported in the spectrographic analysis have been used in the calculations instead of the true values. To avoid possible confusion and to facilitate these calculations, a description of the values that should be used is given in Appendix III.

So far the statistical studies have been used chiefly as a means of identifying anomalous samples. It would facilitate interpretations if more samples were collected in duplicate, and if more analyses were repeated. The data, which can be treated statistically, would indicate reliability of the results. This procedure may avoid prolonged investigations of questionable or unimportant anomalies.

AID PARTICIPATION IN THE GEOCHEMICAL PROGRAM

Continuing assistance to the chemical laboratory is undoubtedly the most useful service that AID can provide to the geochemical exploration program. The guidance given by L. S. Rader, Jr., A. T. Myers, and Ray Havens was most useful in establishing these laboratories. Such visits by experienced chemists should continue so the laboratory in Bogotá can have access to the latest improved analytical techniques of the USGS.

AID assistance seems essential for obtaining chemical supplies. For two months prior to August 10, 1971, the spectrograph was not operating for lack of film. Operations resumed when A. T. Myers mailed a 6-week supply from Denver. Even after Ingeominas devises a better way of obtaining such supplies, it will be most helpful for them to have samples of new chemicals or equipment that may facilitate their work.

As Ingeominas is deeply involved in geochemical exploration, it seems advisable that geologic projects in the AID program should stress geochemistry. Specific suggestions for the Chocó platinum district and the California gold district have been made in this report. Possibly the AID program could help in additional investigations of igneous intrusions.

Geochemical exploration in Colombia could advantageously form a part of both the proposed laterite and the remote-sensing projects of AID.

The training program deserves particular attention. The latest compilation (July 1971) of USGS in-service trainees lists 30 participants from Colombia, of which about 25 came from Ingeominas. These include one chemist, Sr. Emmanuel Hernandez S. (who has now left Ingeominas) and only one geologist, Sr. Andrés Jimeno V., who had training in geochemical exploration. More training in this subject seems desirable.

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APPENDICES

APPENDIX I. SAMPLING METHODS

Stream sediment samples

Sampling of stream sediment requires care because several types of material are present in the stream bed. The coarsest material usually is present in bars, and finer material is in the pools between bars. Fine material may also be present along the edge of the stream channel where it has been deposited by floods. Such material consists mostly of silt and fine sand. Care should be taken to avoid local material such as soil and colluvium along the banks of the stream. Such material, which is usually identifiable from its high clay content, does not truely represent the drainage basin upstream.

In most stream-sediment sampling the sample is placed in a cloth bag or wrapped in paper (not put in a plastic bag as is done in Colombia). I have provided Ingeominas with samples of paper bags in which samples can dry without being opened. When dry the sample is sieved to minus 80 mesh. If fine material is lacking in the stream bed, coarser sizes can be collected. A coarse size (eg. minus 10 mesh) should be pulverized before analysis. Stream-sediment samples are suitable for analysis for copper, lead, and zinc by atomic absorption. Molybdenum can be determined colorimetrically.

The heavy minerals obtained from pan concentrates are commonly analyzed spectrographically. They are more suitable for tracing some metals, such as tungsten and tin. Unless these metals are of primary importance, it is suggested that the silt samples be analyzed and the results interpreted before any pan concentrates are analyzed.

Soil samples

In geochemical prospecting, the surface soil or A horizon is usually sampled unless it has been proven by special study that a deeper horizon must be used. The A horizon generally represents maximum dispersion from weathering ore bodies. The lower horizons may have a higher metal content locally, but it may be confined to a small area that will be missed by widely spaced soil samples.

Wet soil samples commonly are not sieved in the field. A handful of the wet soil is simply wrapped in newspaper or other absorbant paper. The sample number can be written on the outside of the package with a ball-point pen. As soon as possible the packages are spread out on a table in a dry room. Before they dry thoroughly they are soft and can be crushed by squeezing the paper package. Eventually they should be sieved to minus 80-mesh. If allowed to dry completely before crushing, hard lumps of soil may make crushing difficult.

Soil samples commonly are spaced at 30- to 50-meter intervals, and their locations are noted on a simple pace-and-compass map when collected. For interpretation of these samples it is useful to have on the map the location of prospects, geologic features, houses, trails, and other landmarks. As soil continually disperses downhill, it is also useful to have some indication of the land slope. I demonstrated the preparation of such maps several times in Colombia. The value of such maps becomes obvious if one of the samples is found to be anomalous. With the aid of the map, the place can be revisited for additional sampling and mapping.

Water samples

Water samples should be collected if possible when the water is clear and does not require filtration. Spring water is usually clear; waters from small streams usually are clear except during and shortly after rains.

Natural waters are a dilute solution and objectionable changes may take place in their trace element composition before they can be analyzed. To minimize such changes water samples commonly are collected in polyethylene bottles and analyzed in a nearby laboratory within a few days after collection.

During geochemical exploration, water samples commonly are analyzed for total heavy metal, pH, and sulfate. Additional tests may be made for molybdenum or uranium if desirable.

APPENDIX II. ANALYSIS BY THE TOTAL HEAVY-METAL GEOCHEMICAL PROSPECTING TEST

Dithizone tests for total heavy metal

Dithizone is an intensely colored organic compound widely used in trace analysis. Colorimetric tests using this sensitive reagent have proven to be especially useful in geochemical exploration. In the general purpose or total heavy-metal test, dithizone will detect any zinc, copper, or lead in anomalous amounts. It can be used for either water, stream sediment, or soil. Thus it can readily identify samples that are anomalous with respect to any one of these metals.

The total heavy-metal test as applied to soil or sediment has evolved into two different forms. One form, the so-called cold test, is designed to be used at the sample site when the sample is collected. This form of the test gives results immediately, which is a great advantage in some circumstances. The second form of the test requires digestion in boiling acid; it is more suitable for analyzing batches of 20 to 50 samples in a temporary field laboratory. The second form permits the samples to be dried and sieved so that the portion to be analyzed can be measured more accurately. When using the second form, field work consists simply of collecting samples; they are analyzed a few days later when convenient. From experience with both types, in training students, I prefer the second type for general field use. It is the type described below.

The procedure as described herein contains several improvements over any published descriptions. The 1.0 M hydrochloric acid used in the test on soil or sediment is a compromise between a strong acid attack and a mild leach solution. Not enough acid is used to digest a sample rich in carbonate (such as limestone). Better procedures can be found for some samples, but this one appears to be satisfactory for most.

Dithizone solutions

Dithizone solutions are prepared in the field from dithizone-impregnated filter papers which were previously prepared in the laboratory as follows: Dissolve 200 mg of dithizone in 100 ml of chloroform. With an automatic pipette, pipette 2 ml of this solution on a filter paper so that when dry each paper contains 4 mg of dithizone. A supply of these papers is taken to the field wrapped in a plastic bag to protect them from oxidation. The dithizone papers should last for several months without deterioration.

For use in the field the dithizone is dissolved in carbon tetrachloride. Carbon tetrachloride of A.C.S. grade normally is satisfactory for use. Poor grades of carbon tetrachloride contain impurities that oxidize and decompose the dithizone. Within an hour or so the green color of the dithizone will fade to a pale yellow. To test for fading, use several ½-inch squares cut from the dithizone-impregnated paper. Dissolve in the carbon tetrachloride to be tested and set aside for several hours. Compare with a freshly prepared solution or with solutions prepared from other batches of carbon tetrachloride. Heat or

sunlight will accelerate fading. If fading is rapid the carbon tetrachloride can be purified by distilling in a Pyrex still. Some chemists report that it can be purified by shaking with sulfuric acid followed by shaking with demineralized water.

In the field a fresh dithizone solution is prepared daily by soaking one paper in 200 ml of carbon tetrachloride. Do not permit the carbon tetrachloride to come in contact with the fingers or it will dissolve contaminating oils from the skin. For accurate work the volume of the carbon tetrachloride used can be adjusted so that 3 micrograms of zinc will yield a purple color when shaken with the dithizone solution and buffer, as when making the total heavy metal test. Testing with the standard zinc solution can be repeated to find out how long the dithizone solution will last under field conditions.

Total heavy metal in water

1. Place 50 ml of water sample in a glass-stoppered cylinder[1/].
2. Add 5 ml of dithizone solution (4 mg. Dz in 200 ml CCl_4).
3. Add 3 drops of buffer[2/].
4. Cap and shake for 30 seconds. Compare color of organic phase with similar colors made with zinc standards or estimate zinc equivalent from table below:

Color of Dz Solution	Zn equivalents (micrograms)	Sample concentration in ppb for 50 ml of sample
Green	½	10
Blue green	1	20
Blue	2	40
Purple	3	60
Reddish purple	4	80
Purplish red	5	100
Red	6 or more	120 or more

5. If color is red, repeat test using less water sample and/or more dithizone solution until zinc equivalents are determined. Calculate number of micrograms of metal in one liter of sample which is equal to ppb (parts per billion)[3/]

1/ A glass culture tube with a plastic screw cap can be used in the place of a cylinder. Cleanse with pure water and dithizone solution before use.

2/ Prepare by dissolving 61.2 gms of sodium acetate ($NaC_2H_2O_2 \cdot 3H_2O$) and 3.0 ml glacial acetic acid in 75 ml of water. Purify with dithizone solution and dilute to 250 ml.

3/ Complete instructions can be found in U.S.G.S. Bulletin 1152.

Total heavy metal in soil or sediment

1. Place one scoopful (50 mg) of sample in a clean, dry test tube.
2. Add 1.0 ml of 1.0 M HCL to each sample and boil each briefly over a flame. After all samples have been boiled once boil each one again. Mix while adding 9 ml of pure water. Permit suspended sediment to settle.
3. Place 5 ml of dithizone solution[1/] and 5 ml of buffer[2/] in a colorimetric tube, shake violently for 10 seconds. Discard solution and repeat if any change in color indicates an unclean tube.
4. Transfer 5 ml of clear test solution to the colorimetric tube. Cap tube and shake vigorously for 30 seconds. Compare color of organic phase with zinc standards or estimate equivalent from table below:

1/ Prepare dithizone solution by dissolving 4 mg of dithizone in 200 ml of carbon tetrachloride. For greater accuracy adjust solvent volume so that 3 micrograms of zinc standard will yield a purple color.

2/ Prepare buffer by dissolving 82 gm of sodium acetate ($NaC_2H_3O_2 \cdot 3H_2O$) and 10 grams of ammonium fluoride (NH_4F) in pure water. Purify with dithizone solution and dilute to 1.0 liter.

Color of dithizone solution	Zinc (micrograms)	Sample concentration in ppm for 5 ml of solution
Green	½	20
Blue green	1	40
Blue	2	80
Purple	3	120
Reddish purple	4	160
Purplish red	5	200
Red	6 or more	240 or more

5. If color is red repeat test using a smaller aliquot and/or more dithizone solution. Determinations are most accurate near the purplish mid-color. Calculate number of micrograms of metal in one gram of soil which is equal to parts per million.

APPENDIX III. STATISTICAL TREATMENT OF DATA

Geochemists commonly use statistics as a means of summarizing data and identifying anomalous samples. In Colombia, statistics has been used in various ways so that it is difficult to compare results from one region with another. Some investigators calculate the geometric mean and standard deviation; others use the arithmetric mean and standard deviation. These yield quite different results. I was surprised to see some histograms made of bars of different widths. Questioning disclosed some confusion as to the meaning of the values reported in the spectrographic analysis. Although a brief explanation is given by Ward and others (1963), it is explained more fully here.

The values, such as 10, 15, 20, 30, 50, 70, etc., which are reported in a spectrographic analysis are not all the true values. Some of them have been rounded for convenience. The true values are given in table 1 along with their logarithms. From this table it can be seen that the true values have been chosen so that their logarithms increase by equal intervals. The true class limits are also given in this table along with their logarithms. When these class limits are used to make histograms, all the bars will have equal widths. In calculating a geometric mean or standard deviation, the logarithm of the true midpoint should be used. This is easy for spectrographic data. It also can be used for data obtained by atomic absorption, if the true class limits are used to group the values.

Table 1.--Relationship between values reported in spectrographic analyses, the true values, and the corresponding logarithms

Class midpoints		Class limits	Logarithms
Reported (ppm)	True		
		121	2.083
100	100[1/]		2.000
		82.6	1.917
70	68.1		1.833
		56.2	1.750
50	46.4[1/]		1.667
		38.3	1.583
30	31.6		1.500
		26.1	1.417
20	21.5[1/]		1.333
		17.8	1.250
15	14.7		1.167
		12.1	1.083
10	10.0[1/]		1.000
		8.3	0.917

1/ These values correspond to the spectrographic standards.

Calculating means and standard deviations is time consuming and can be avoided simply by using the median to indicate the average. The median is the middle value (half are higher and half are lower). It is the same whether histograms are prepared on a geometric scale or on an arithmetic one. Care should be taken in plotting to use the class limits in preparing histograms and cumulative curves (some workers used the class midpoints). If cumulative curves are plotted on logarithmic probability paper, the median can easily be determined graphically. Likewise a threshold can be selected at any convenient value. For example, the 90th percentile can be used as the threshold, if it is decided to identify the highest 10 percent of the samples as anomalous.